

Investigation of the oxidation mechanism of limonene photosensitized by imidazole-2-carboxaldehyde and leading to aerosol growth

S. Rossignol, L. Tinel, K. Aregahegn, L. Fine, B. Nozière and C. George

Université de Lyon, Université Lyon 1, CNRS, UMR5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Villeurbanne, F-69626, France

Keywords: imidazole-2-carboxaldehyde, photosensitized reaction, aerosol growth, limonene.

Presenting author email: stephanie.rossignol@ircelyon.univ-lyon1.fr

Recent studies have revealed the significant formation of light absorbing materials, including imidazole and its derivatives, in aqueous aerosol mimics in the presence of both ammonium sulphate and glyoxal (Galloway et al. 2009; Nozière et al. 2009; Yu et al. 2011; Kampf et al. 2012). Besides the potential impact on radiative properties of secondary organic aerosols, our team has shown that imidazole-2-carboxaldehyde (IC) can act as a photosensitizer, initiating aerosols growth in the presence of gaseous limonene and UV/visible light (Aregahegn et al., abstract submitted to the EAC 2013).

This work focuses on the characterisation of the chemical mechanism leading to this aerosols growth, and on the major products identification.

The molecular composition of organic/aqueous solutions exposed to UV/visible light and containing IC and limonene is followed in time by HR-ESI-MS in positive and negative modes. Limonene consumption is followed by HPLC-UV.

HR-ESI-MS and UPLC-HR-ESI-MS analyses are performed in parallel on IC/ammonium sulphate aerosols exposed to gaseous limonene and UV/visible light during flow tube experiments and collected onto Teflon filters subsequently solvent extracted.

In addition,, the lifetime of the triplet state of IC in aqueous/organic solutions in the presence of different terpenes is measured by means of photolysis experiments and compared in order to explain the first steps of the photosensitized reaction.

First HR-ESI-MS results of the irradiation of organic solutions containing IC and limonene, show the formation of the major "traditional" limonene oxidation products (e.g., coming from gas phase limonene ozonolysis, Leungsakul et al. 2005): limononaldehyde, keto-limononaldehyde, limonic acid, limonic acid ... Hundreds of other oxygenated species are however detected, typically with a number of carbon atoms ranging from 4 to 20 and with O/C ratios ranging from 0.2 to 0.7. Monomers and dimers of limonene oxidation products are observed but species with lower carbon numbers than monomeric compounds are predominant. Moreover, and surprisingly, the production rates of all products tend to increase with reaction time and the limonene consumption presents an apparent linearity. These preliminary findings would suggest, under our experimental conditions, an oxidation mechanism initiated by a relatively slow photosensitized process (e.g., electron transfer from limonene to the triplet state of IC, which formation is confirmed by laser photolysis

experiments), followed by an increase of radicals in the solution leading to an extended limonene oxidation. The UV radiation, and/or the low concentration of reactants, are susceptible in our context to limit the formation of oligomers (Bateman et al. 2011) and promote fragmentation pathways.

Alongside, the preliminary results of the analysis of IC/ammonium sulphate aerosols exposed to both limonene and UV light in flow tube experiments confirm the presence of limonene oxidation products and, in the same time, confirm that the observed aerosol growth is due to limonene multiphase oxidation reactions initiated by a photochemical mechanism linked to the presence of IC.

Through this elucidation of the photosensitized oxidation mechanism of limonene by IC, this study attempts to provide a new insight in how light activated chemical reactions at the gas/aerosol interface can be of atmospheric significance and, potentially, of overall environment relevance, at other air/condensed phase surfaces, such as air/water interfaces.

- Bateman, A. P., Nizkorodov, S. A., Laskin, J., et al. (2011) *Phys. Chem. Chem. Phys.* **13**(26) 12199-12212.
- Galloway, M. M., Chhabra, P. S., Chan, A. W. H., et al. (2009) *Atmos. Chem. Phys.* **9**(10) 3331-3345.
- Kampf, C. J., Jakob, R. and Hoffmann, T. (2012). *Atmos. Chem. Phys.* **12**(14) 6323-6333.
- Leungsakul, S., Jaoui, M. and Kamens, R. M. (2005) *Environ. Sci. Technol.* **39**(24) 9583-9594.
- Nozière, B., Dziedzic, P. and Córdova, A. (2009) *J. Phys. Chem.* **113**, 231-237
- Yu, G., Bayer, A. R., Galloway, M. M., et al. (2011) *Environ. Sci. Technol.* **45**(15) 6336-6342.